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**210) IV-B-17**

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## How MMT Causes Plugging of Monolithic Converters

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Congress and Exposition  
Cobo Hall, Detroit  
February 27-March 3, 1978



**SOCIETY OF AUTOMOTIVE ENGINEERS, INC.**  
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## How MMT Causes Plugging of Monolithic Converters

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VEHICLE TESTS (1)\* have shown that, with a driving cycle more severe than the new-car certification schedule, a monolithic converter attached to the exhaust manifold can become plugged with deposits of manganese oxide when the fuel contains the antiknock additive methylcyclopentadienyl manganese tricarbonyl (MMT). The deposits restrict the exhaust flow, causing a deterioration in vehicle drivability and performance.

There have also been other reports of monolithic converter plugging related to MMT in the fuel (2).

Although extensive tests have been conducted with MMT (3,4), little was known about the mechanism of converter plugging. Consequently, we undertook an engine-dynamometer study to investigate some of the variables which might affect plugging. The need for this study was indicated by both the vehicle test results, just mentioned, and the rapidly

changing MMT situation, which is summarized in the next two paragraphs.

The use of MMT in unleaded gasoline has been increasing over the past two years. The 1977 summer MVMA National Fuel Survey (5) showed that about 40 percent of the 232 unleaded gasolines which were sampled contained MMT at concentrations of at least 0.003 g Mn/L. The average concentration of MMT in those gasolines was 0.010 g Mn/L. The use of MMT in unleaded gasoline reportedly provides economic and energy conservation benefits for refiners (6).

During the past year, there have been several significant developments with respect to the use of MMT. In June 1977, Ethyl Corporation, the sole supplier of MMT, reduced the maximum recommended level from 0.033 to 0.017 g Mn/L, although very few gasolines at that time contained more than 0.017 g Mn/L. The California Air Resources Board banned MMT from gasolines sold in that state beginning September 8, 1977. Finally, the August 1977 amendments to the Clean Air Act imposed a limit of 0.017 g Mn/L after November 30, 1977, and

\* Numbers in parentheses designate References at end of paper.

### ABSTRACT

Monolithic oxidation converters can become plugged with manganese oxide deposits when the gasoline contains the antiknock additive MMT. Engine dynamometer studies showed that the rate of converter plugging depended on the catalyst inlet temperature and the concentration of MMT in the fuel. Converter plugging was not affected by base fuel or engine oil compo-

sition, and it occurred as readily with a bare monolithic support containing no catalytic material as with a production catalyst. Monolithic converter plugging appears to be a physical, rather than a chemical phenomenon, in which the manganese oxide collects primarily on the inlet edge of the converter.

banned the use of MMT in gasoline entirely after September 15, 1978, unless the Environmental Protection Agency grants a waiver.

This report discusses our engine dynamometer study of monolithic converter plugging. The experimental details are mentioned first. Then, the results are presented, along with a discussion of their significance. Based on those results, a mechanism of monolithic converter plugging is suggested.

#### EXPERIMENTAL PROGRAM

**TEST ENGINES** - Two production 1977 Chevrolet 4.1-L six-cylinder engines with California emission control systems were used. The engines had heated intake air control, exhaust gas recirculation (EGR), and secondary air injection (AIR) at the exhaust ports, and were equipped with both monolithic and bead-type catalytic converters. The monolithic converter, shown in Figure 1, contains two monoliths composed of a cordierite substrate covered with alumina on which the platinum and palladium are deposited. Because of repeated

plugging, the bead-type converter was removed from one engine part way through the program and replaced by a large gate valve to simulate the pressure drop across the converter. The early fuel evaporation (EFE) valve, which normally directs exhaust gas under the carburetor to improve cold-start driveability, was disconnected so that the exhaust flow route was always in the warmed-up mode. The choke was clamped in the full-open position at all times. These modifications were made because the tests were to be run at warmed-up steady-state conditions, and these warm-up devices were not needed. One engine was connected to an electric dynamometer, and the other to a water-brake dynamometer.

**FUELS** - The base fuel for most of the tests was the Chevron unleaded gasoline (UL77CQ), containing the detergent additive F-310 used in mileage accumulation during the new-car certification procedure. This fuel was chosen because its properties were carefully controlled and remained fairly constant, it was easily obtainable in large quantities, and it had been used for the vehicle tests (1) in which catalyst plugging occurred. A commercial unleaded gasoline (Fuel A), available in the Detroit area during the first few months of 1977, was used for some tests. Typical properties of the fuels are shown in Appendix A. MMT was added to the base fuels in the desired concentrations.

**ENGINE OILS** - A commercial SE-quality (SAE viscosity 10W-40) engine oil was used in most of the tests. An experimental ashless oil, containing no zinc, calcium, magnesium, or phosphorus, was used in two tests.

**ENGINE MAINTENANCE** - The engine oil, oil filter, spark plugs, and catalytic converters were replaced before each test. The oil was changed approximately every 100 hours, if the test extended beyond that time, and the oil filter was replaced every 200 hours. The ashless oil was changed every 50 hours, because it did not provide adequate antiwear protection. Spark plugs were changed during a test only if misfire occurred, as determined by engine hydrocarbon emissions.

**TEST PROCEDURE** - In some earlier work at Ethyl Corporation (3), exhaust temperature was identified as an important factor in the plugging of an oxidation catalyst. Therefore, exhaust temperature near the catalyst inlet was controlled in this study. With the engine connected to the electric dynamometer, exhaust temperature was controlled by setting the engine speed, and adjusting the throttle (manifold vacuum) to obtain the desired temperature. The manifold vacuum remained fairly constant throughout any given test, and exhaust temperature control was excellent. Power output was monitored, but not controlled. With the engine connected to the water-brake dynamometer, an adjustment of the throttle changed both speed

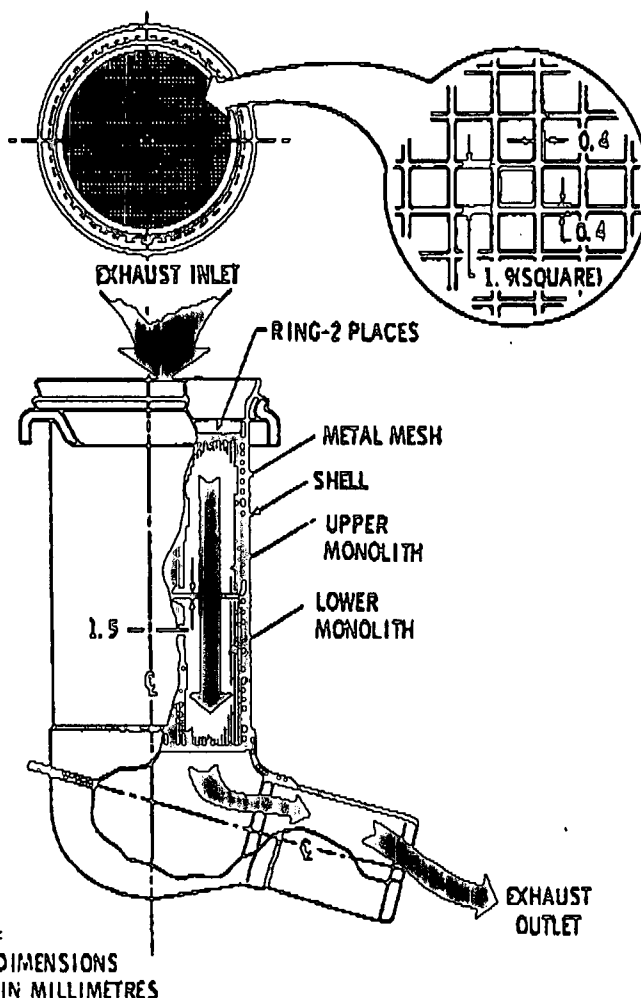


Fig. 1 - Monolithic converter

and manifold vacuum, and temperature control was satisfactory but not quite so good as with the electric dynamometer facility.

The following temperatures were monitored, using shielded thermocouples:

1. Coolant outlet temperature at the thermostat housing. The thermostat was removed, and the coolant temperature was controlled externally to 88°C.

2. Oil sump temperature. This temperature varied with the engine operating conditions.

3. Room air temperature.

4. Fuel temperature at the fuel flow meter.

5. Exhaust gas temperature in the exhaust manifold, 13 mm above the inlet edge of the monolithic catalyst. [This is the same location at which the temperature was measured in the vehicle tests (1).]

6. Bed temperature near the middle of the bead-type converter. This temperature was measured during only a few tests.

Exhaust pressure was measured with a mercury manometer at three locations: 1) at the top of the exhaust manifold, directly above the monolithic converter; 2) in the exhaust pipe near the monolithic converter exit; 3) after the bead-type converter.

Exhaust emissions were measured at the same locations as the exhaust pressure. A Beckman flame ionization analyzer, calibrated with propane, was used to determine hydrocarbon concentrations. Carbon monoxide and carbon dioxide were measured with Beckman infrared analyzers. Oxygen concentrations were measured with a Beckman oxygen analyzer.

A fuel flow meter was used to accurately measure the fuel consumption of one engine. The fuel consumption of the other engine was estimated, when necessary, from the volume of fuel in the storage tank before and after a test.

Engine manifold vacuum was measured with a mercury manometer.

## RESULTS AND DISCUSSION

This section first presents the results of the initial converter plugging tests and the analyses of the converter deposits from those tests. Next, the investigation of several factors which might affect converter plugging is described. Finally, a mechanism of monolithic converter plugging is suggested.

**INITIAL CONVERTER PLUGGING TESTS** - The relationship of exhaust gas (catalyst inlet) temperature to engine operating conditions was determined during a 10-hour engine break-in with a clear fuel containing no MMT. The first converter plugging test was run with fuel containing MMT at a concentration of 0.033 g Mn/L and an exhaust gas temperature of 843°C. This temperature was chosen because of a report (3) that the threshold temperature for converter plugging was about 816°C. (The engine conditions required to produce an exhaust temperature of 843°C were 3 000 rpm and 15.2 kPa intake manifold vacuum, equivalent to a vehicle operating at about 115 km/h at slightly more than road load.) Under these test conditions, the converter plugged. Figure 2 shows that beginning with the clean engine (no manganese deposits), the pressure

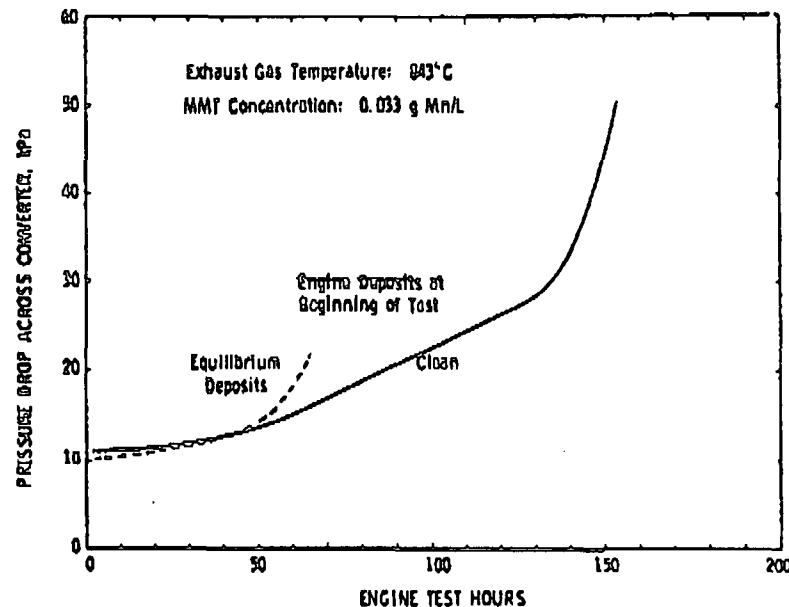


Fig. 2 - Effect of engine deposits on monolithic converter plugging

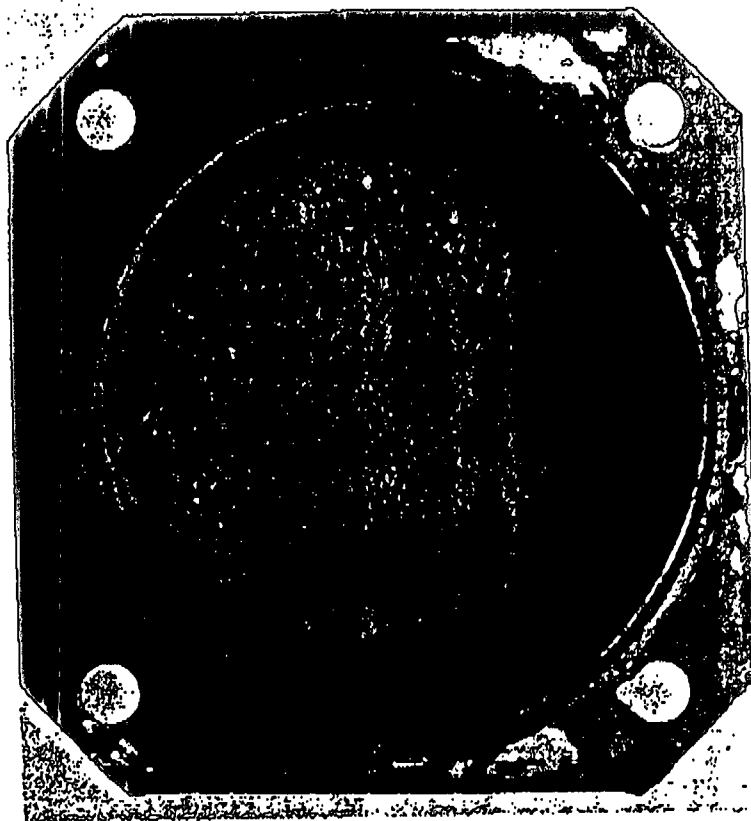


Fig. 3 - Monolithic converter plugged with manganese oxide deposits

drop across the converter increased slowly at first, and then more rapidly. After about 140 hours, the exhaust restriction increased very rapidly. At 153 hours, the pressure drop across the converter was approaching five times its initial value, and the test was stopped. Approximately 80 percent of the inlet face of the upper monolith was plugged with deposits, as shown in Figure 3. Deposits were also found at the inlet edge of the lower monolith, but none of the channels were plugged.

The very high exhaust pressure near the end of the test resulted in some minor engine problems, such as damage to the EGR valve and overheating of the Air Injection Reactor (AIR) manifold. (The AIR pump could not force air into the exhaust manifold.) Therefore, it was decided that in subsequent tests, a doubling of the pressure drop across the converter would be sufficient evidence of converter plugging. From Figure 2, it can be seen that the pressure drop in the test beginning with the clean engine doubled in about 95 hours.

After replacing the catalytic converters and spark plugs and performing the other maintenance as described earlier, another test was run under the same conditions, except that the deposits were not removed from the combustion chambers and manifold. Presumably, those deposits had reached equilibrium. In this test, the converter plugged (the pressure drop

doubled) in about 65 hours, as shown in Figure 2. This was only about two-thirds the time required for plugging when starting with a clean engine. However, the shapes of the pressure drop curves were similar. A longer time was required for converter plugging when beginning with the clean engine presumably because more of the deposits remained in the engine.

All subsequent tests were run without removing the engine deposits.

**DEPOSIT COMPOSITION** - The reddish-brown deposits which plugged the converters were located just at the inlet edge. They extended only about 1 mm down into the channels of the monolith, and they had also built up above the edge of the monolith. Some of these deposits were removed and analyzed. The average results for the two tests described above are shown in Table 1.

The manganese came from the MMT. The phosphorus, zinc, and calcium undoubtedly came from the engine oil, and the iron from the engine itself. X-ray diffraction analysis indicated that the deposits were primarily  $Mn_3O_4$ . No  $MnO$  was identified. Electron microprobe analysis of the monolith revealed that the alumina coating on the cordierite substrate was not broken, and there was no evidence of any reaction between the manganese oxide and the cordierite.

a few channels of the converter were plugged. This result demonstrates that converter plugging is not a problem when the fuel does not contain MMT. After the usual engine maintenance, but without removing any combustion chamber deposits, a test was conducted using Fuel A containing MMT at a concentration of 0.034 g Mn/L. The pressure drop across the monolithic converter doubled in about 142 hours. Unfortunately, the average exhaust gas temperature was only 830°C, rather than the desired 843°C. As will be seen later, this temperature difference was sufficient to have a considerable effect on the rate of converter plugging.

Another test was run with Fuel A containing 0.034 g Mn/L, this time at an exhaust gas temperature of 843°C. The manganese deposits in the engine were assumed to have reached equilibrium by the time this test began. The converter plugged (pressure drop doubled) in 69 hours, in good agreement with the 65 hours required when using Chevron fuel under similar conditions in the other engine. Therefore, the base fuel and additive package did not affect the rate of converter plugging.

#### Manganese Concentration in the Fuel -

Since monolithic converter plugging is caused by a collection of manganese oxide deposits on the inlet edge of the monolith, the rate of plugging should be a function of the amount of MMT in the fuel. A number of tests had already been run with MMT concentrations of 0.033 g Mn/L. Therefore, additional tests were con-

ducted under similar conditions, but with MMT concentrations of about 0.016 and 0.008 g Mn/L. Figure 4 shows that the relationship of average plugging time to the reciprocal of the fuel manganese level is essentially linear - plugging time increases as the MMT concentration decreases. Thus, plugging time is inversely proportional to the concentration of MMT in the fuel.

Exhaust Gas Temperature - Passenger cars with the 4.1-L engine are likely to experience exhaust gas temperatures as high as 843°C for only a small portion of the time they are operating (1). Therefore, tests were also run at lower exhaust gas temperatures, specifically 706°C, 741°C, and 788°C. (The average exhaust gas temperature of several 1977 California Chevrolet Impalas with 4.1-L engines, operating at 88 km/h road load, was about 705°C.) In the lower part of this temperature range, e.g., 706°C and 741°C, the exhaust flow rate is low enough so that the monolithic converter has substantial excess flow capacity. Therefore, as deposits accumulate on the converter, the pressure drop may not increase as rapidly as it does at higher exhaust temperatures and flow rates. Since the parameter of interest in this study is the rate of deposit accumulation on the converter, a more useful, although more difficult way to compare converter plugging rates when different engine operating conditions are involved is on the basis of the percentage of the converter inlet face which is blocked by deposits. The converter was removed

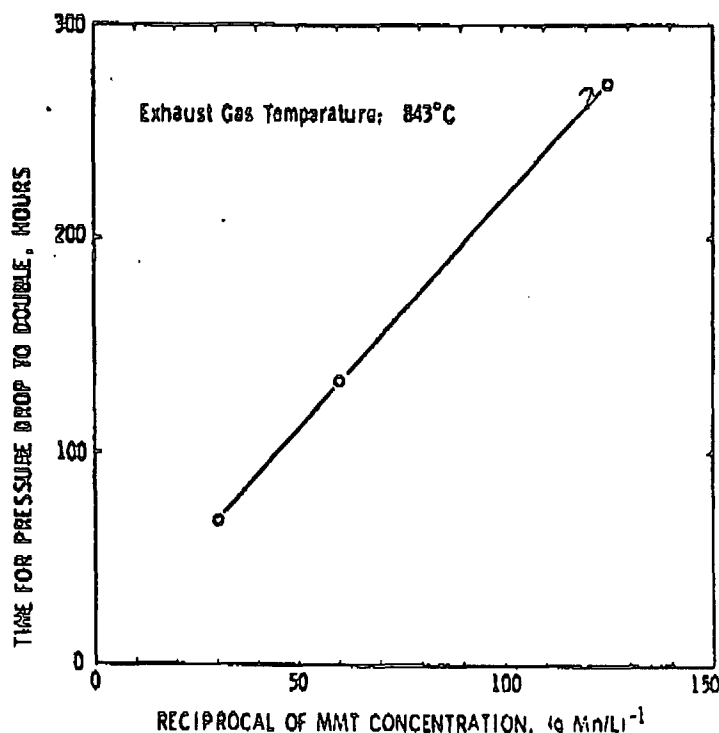


Fig. 4 - Effect of MMT concentration on the time required to plug a monolithic converter

Table 3. Variation of Fuel Consumption with Exhaust Gas Temperature

Exhaust Gas Temp., °C	Fuel Consumption, kg/hr
706	10.7
741	14.6
788	15.1
843	16.0

was reduced from 843°C to 741°C, fuel consumption, and hence the rate of manganese consumption, declined by about 9 percent, while the time required to plug the converter increased nearly 600 percent. Comparing the data at 843°C and 706°C, fuel consumption declined by 33 percent, but plugging time increased by about 1500 percent.

To determine whether the distribution of manganese oxide deposits along the length of the catalyst varied with temperature, tests were run for 11 hours and for 25 hours, at exhaust gas temperatures of 713°C, 780°C, and 843°C, a total of six tests. No plugging occurred, except for a very small amount in the 25-hour test at 843°C. It has been reported (7) that lead accumulation decreases logarithmically along the axis of a monolithic converter. Consequently, in preparing our samples of monolith for analysis, the sectioning along the monolith axis was performed in a manner that reflected the expected contaminant profiles. The upper and lower monolithic sections, each 76 mm in length, were removed from each of the six converters. A 13-mm x 13-mm x 76-mm section was carefully cut from near the center of each monolith. This small section was then cut into the following five lengths: 0-6 mm, 6-13 mm, 13-25 mm, 25-44 mm, and 44-76 mm. Each segment was ground and analyzed for manganese, zinc, and phosphorus. Figure 7 shows the results of the 11-hour test at 843°C. The profiles were similar for the other tests. The concentrations of contaminants were greatest near the inlet edge of the monolith, decreasing with distance into the monolith. However, the plots of the logarithm of the contaminant concentration as a function of distance along the monolith (Figure 7) were curved rather than straight, indicating that the decrease was not logarithmic as had been reported for lead contamination. The significant enrichment of contaminants near the inlet edge of the monolith suggests that a unique deposition process was occurring there. The contaminant profiles were similar in shape for both the upper and lower monolithic sections. The profiles were also similar for all three temperatures, indicating that the deposition mechanism was probably the same, at least in the early stages of the test.

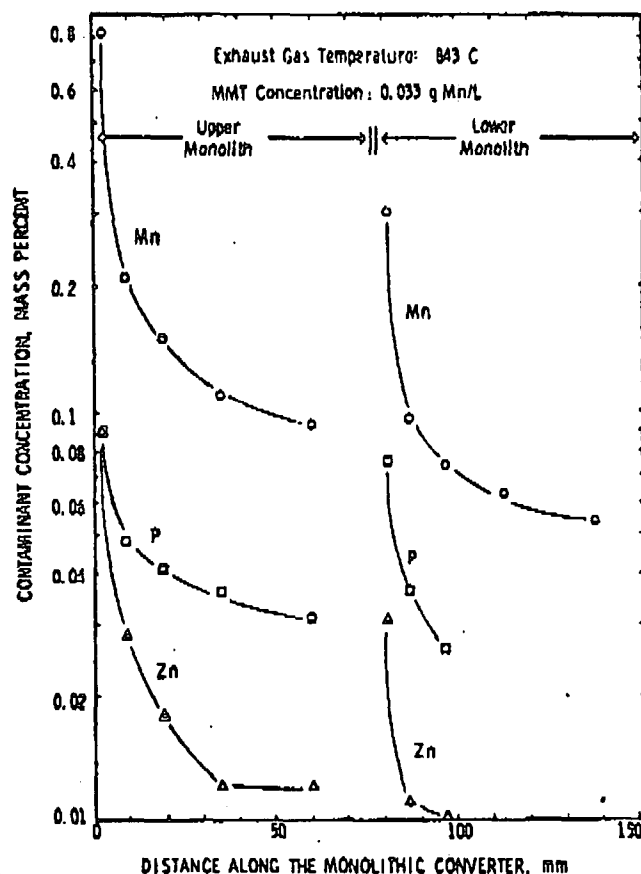


Fig. 7 - Distribution of contaminants along the converter in 11 h

Since hydrocarbons and carbon monoxide are oxidized in the catalytic converter, the temperature in the catalyst bed was expected to be higher than the inlet exhaust gas temperature. To confirm this, simultaneous temperature measurements were made in the exhaust manifold at the usual location 13 mm above the inlet edge of the catalyst, and at a point in the catalyst bed 25 mm below the inlet edge of the catalyst and 13 mm from the side of the converter nearest the engine. The catalyst bed temperature was, indeed, higher than the exhaust gas temperature, ranging from an increase of 56°C at an exhaust temperature of 871°C to an increase of 103°C at 713°C exhaust temperature. An even greater temperature difference existed between the exhaust gas temperature, and the temperature of the catalyst bed 25 mm below the inlet edge and near the longitudinal axis of the converter.

If increased deposit collection on the catalyst were due to an increase in temperature alone, then deposits should build up more rapidly near the center of the bed than at the inlet edge. Since that did not occur, some other factors must be involved.

"Noncatalytic" Converter - Examination of the plugged converters from the initial tests had failed to reveal any chemical interaction between the manganese oxide and the converter.



The alumina wash coat had not been broken to expose the cordierite, so there was no opportunity for the manganese to react with the substrate. To further explore possible interactions between the manganese oxide and the converter, a test was run with a converter containing monolithic elements of bare cordierite. The alumina wash coat and the catalyst material (platinum and palladium) had not been applied to the support. With an exhaust gas temperature of 843°C and a fuel manganese level of 0.033 g Mn/L, the converter plugged in 64 hours, essentially the same as earlier tests with a production converter. Thus, the plugging does not depend on the presence of catalytic material or the alumina wash coat.

The temperature of the "nongate" (cordierite only) bed was measured 25 mm below the inlet edge, as had been done with the production converter. At exhaust gas temperatures in the range of 829°C to 857°C, the nongate bed temperature was about 43°C higher than the exhaust gas temperature, compared with a difference of 72°C with the production converter. (The temperature increase was due to the oxidation which occurs at high temperatures. The oxidation may have been helped by the Mn<sub>2</sub>O<sub>3</sub> which accumulated on the support, because manganese oxides are good catalysts for hydrocarbon and carbon monoxide oxidation.) These data further confirm that the exhaust gas temperature, rather than the catalyst bed temperature, is the important factor in converter plugging. This should not be too surprising, since the plugging occurs just at the inlet edge of the converter, and the catalyst temperature at that point is not much higher than the exhaust gas temperature.

#### Air-Fuel Ratio and Exhaust Oxygen Content -

Air-fuel ratios were calculated from exhaust gas analysis. With secondary air injection at the exhaust ports, these calculated ratios were, of course, different from the air-fuel ratios in the combustion chamber, and were generally on the lean side of stoichiometric. (The stoichiometric air-fuel ratio was 14.44). However, the manganese oxide is probably formed in the combustion chamber, before secondary air injection, and so the air-fuel ratio in the combustion chamber may be of greater interest. During some of the tests, the AIR system was disconnected momentarily while the exhaust gas composition was determined. This permitted calculation of the air-fuel ratio in the combustion chamber. In all tests except the one at 706°C, this air-fuel ratio was richer than stoichiometric, generally about 13.4-13.5. Thus, the air-fuel ratio remained essentially constant over a wide range of exhaust gas temperatures, and so the effect of temperature on the rate of converter plugging cannot be attributed to differences in air-fuel ratio. In the test at 706°C, however, the air-fuel

ratio was about 15.4, which is leaner than stoichiometric.

With secondary air injection at the exhaust ports, there was always an excess of oxygen in the exhaust manifold near the catalyst inlet. However, the oxygen level varied with exhaust gas temperature, because of the changes in engine operating conditions required to change the temperature. For example, the exhaust gas in the manifold typically contained about 1.5-2.0 percent oxygen at 843°C, about 3 percent at 788°C, and about 5 percent at 706°C. Although it did not seem likely that this change in excess oxygen with temperature was responsible for the difference in the rate of catalyst plugging, an attempt was made to control the exhaust temperature and exhaust oxygen content independently.

The engine was stabilized at an exhaust temperature of 788°C. Then, the basic spark timing was retarded 8 degrees from the recommended setting, and this increased the exhaust gas temperature to about 843°C. (The throttle had to be opened to maintain engine speed.) However, the exhaust oxygen content ahead of the converter remained at 3.1 percent, essentially the same as the 3.0 percent oxygen observed at 788°C. Under these conditions, the converter plugging time was typical of the 843°C temperature, and was essentially unaffected by the increased amount of oxygen. Again, the exhaust temperature was shown to be the important factor in the rate of plugging, regardless of how the engine conditions were varied to obtain the desired temperature.

Exhaust Particulate Size - An Electrical Aerosol Analyzer was used to determine the size distribution of the particulate matter in the exhaust. The objective of these experiments was to determine whether the size distribution of the manganese oxide particulates changed with temperature. Therefore, it was important to sample the exhaust as close as possible to the location where plugging occurred. Because of high temperatures and exhaust pressures, this is a much more severe sampling environment than is encountered in typical tailpipe particulate measurements. A converter shell, without the monoliths, was modified for the sampling probe. An exhaust gate valve downstream of the converter shell was adjusted to provide the exhaust pressure which would have been present with the normal monolithic converter.

The number distributions for the tests at 704°C and 843°C are shown in Figure 8. The bars indicate the actual measurements of the relative number of particles in each size range, while the line is a computer-generated distribution of particle size based on the measurements. The results for each test are given in relative units, because the total number of particles was not known. Thus, particle size distributions can be compared at

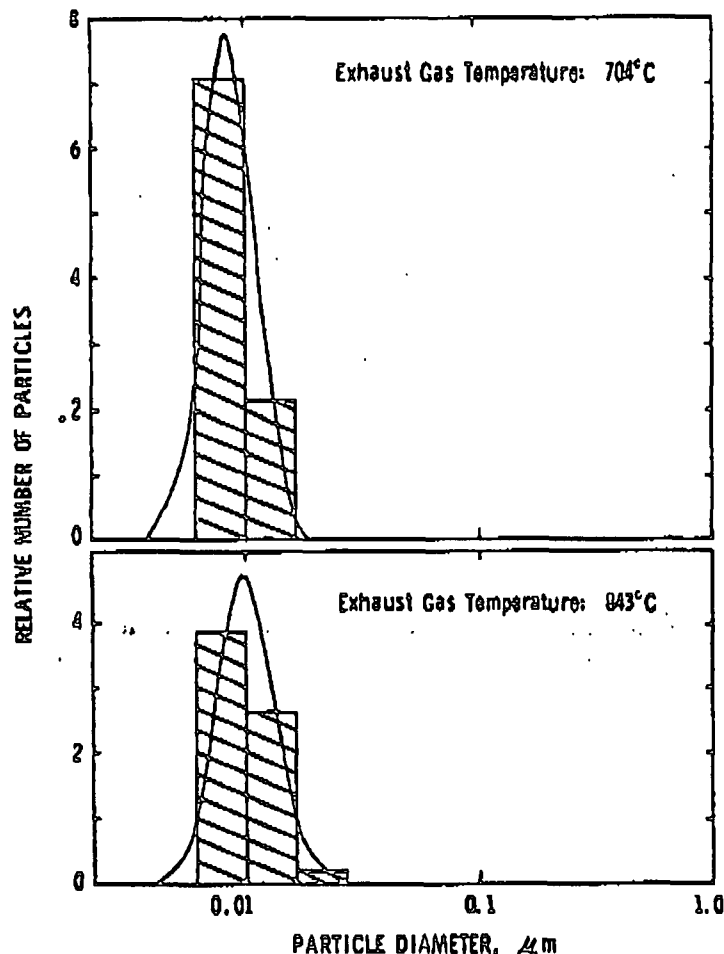


Fig. 8 - Effect of temperature on exhaust particulate size distribution

different temperatures, but the total number of particles cannot. In all tests, the distribution was centered near 0.01 μm particle diameter. There was essentially no difference in particle size distribution over the temperature range of 704°C to 843°C.

**WHY CONVERTERS PLUG** - The MMT concentration in the fuel and the exhaust gas (catalyst inlet) temperature have been identified as the most important factors involved in monolithic converter plugging. The other factors investigated had no effect. Additional information about the converter deposits was needed so that a plugging mechanism might be suggested.

**Melting Temperature of Converter Deposits** - The melting point of pure  $Mn_3O_4$  is reported to be 1705°C (8). However, contaminants can reduce the melting point substantially. If the manganese oxide in the exhaust were to begin melting at a temperature near that of the exhaust gas, some particles could stick to the catalyst surface, and trap other particles which come in contact with them. Consequently, melting point determinations were run on converter deposits from three tests: the 706°C test, an 843°C test with conventional engine oil, and an 843°C test with ashless engine oil.

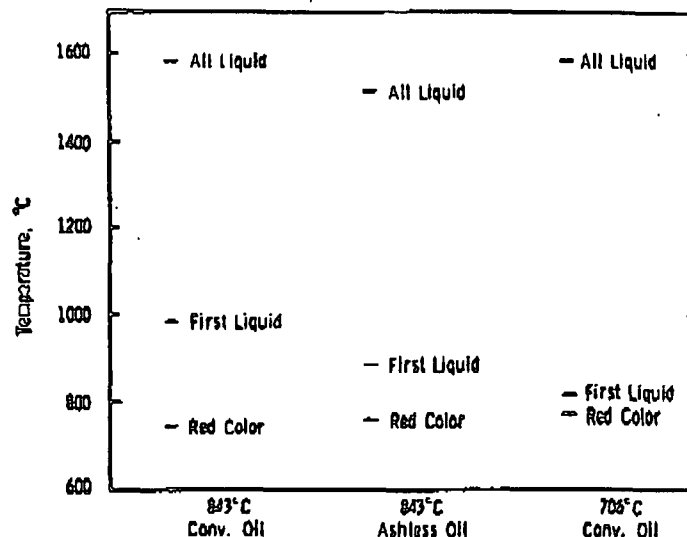


Fig. 9 - Melting temperatures of converter deposits from three tests

A small amount of deposit was placed on a platinum wire hot stage, and observed through a microscope as the temperature was increased from 25°C to 1600°C. The significant observations are shown in Figure 9.

All three samples became bright red at about 750°C to 765°C. The first liquid appeared at temperatures of 820°C to 980°C, and the amount of liquid increased gradually until the samples were entirely melted at 1510°C to 1580°C. The deposits apparently began to melt at temperatures somewhat higher than the exhaust gas temperatures measured in the engine tests. However, the possibility exists that the deposits may have become "sticky" below the temperature at which the first liquid was observed. Furthermore, the melting or sintering temperature of the very small particulate in the exhaust gas stream might be lower than the melting temperature of the converter deposits.

On the other hand, if the true exhaust gas temperature were somewhat higher than the temperature indicated by the shielded thermocouple near the converter inlet, the initial melting temperature of the deposits may have actually been reached. To investigate this possibility, a bare-wire thermocouple was inserted into the exhaust manifold next to the shielded thermocouple, and the two were compared. In all cases, the bare-wire thermocouple indicated a higher exhaust gas temperature. The difference varied from 14°C at an exhaust temperature of 704°C to 39°C at a temperature of 843°C. This means that the exhaust temperatures previously reported as 843°C were actually about 882°C. This is within the melting range of two of the three deposits described in Figure 9. The use of a shielded thermocouple is still justified for most tests, because the bare wire will not

survive very long in the environment of the exhaust manifold. In addition, the vehicle exhaust temperatures (1) were measured with a shielded thermocouple, and so those temperatures can be directly compared with the temperatures reported in this engine study.

A Proposed Plugging Mechanism - Based on the data presented, a mechanism of monolithic converter plugging is suggested. The manganese-containing combustion product of MMT is  $Mn_3O_4$ . This is the most stable oxide when manganese is oxidized in air (9). Other manganese oxides,  $MnO$ ,  $Mn_2O_3$ , and  $MnO_2$ , are converted to  $Mn_3O_4$  at high temperatures in the presence of air (10,11). More specifically,  $Mn_3O_4$  has been reported as the major product in both laboratory (12) and vehicle (3) studies involving combustion of gasoline containing MMT.

The particle size measurements showed that the manganese oxide particles are quite small (about 0.01  $\mu m$  diameter), and they would be expected to pass through the monolithic converter easily. However, the exhaust flow is quite turbulent as it approaches the converter. Of even more importance is the geometry of the exhaust system where the converter connects to the exhaust manifold. The exhaust gases must make a sharp 90° turn, and this probably introduces a substantial transverse element to the exhaust flow as it enters the converter. Some of the manganese oxide particles impinge on the catalyst surface at the converter inlet. If the temperature of either the catalyst surface or the particles themselves is at or above the initial melting or sintering temperature of the particles, some particles stick to the catalyst. The higher the temperature, the "stickier" the deposits become. The deposits continue to grow outward in all directions, reducing the size of the monolith channels. This makes it more difficult for subsequent particles to get into the channels, and the rate of plugging increases.

The exhaust flow becomes laminar within the channels of the monolith, so most of the manganese oxide particles which get past the inlet edge of the catalyst without adhering to it, pass relatively easily through the rest of the converter, even though higher temperatures are encountered.

Some turbulence is generated in the 1.5-mm space between the upper and lower monolithic sections of the converter. In addition, it is extremely unlikely that the channels of the two sections are perfectly aligned. Some of the particles strike and adhere to the inlet edge of the lower section, accounting for the substantial deposits found there.

At the lower temperatures investigated, 741°C and especially at 706°C, very little of the manganese oxide adheres to the catalyst because the melting temperature has not been reached. Deposits accumulate very slowly.

However, some relatively large particles formed in the engine can be dislodged and become wedged in some of the converter channels. (X-ray diffraction analysis showed that the particles were composed primarily of zinc and calcium orthophosphates.) These particles reduce the size of the channel openings and provide a good trap for the manganese oxide. The oxide collects around the larger particles and eventually plugs the channels completely. However, only a small percentage of the channels are plugged in this manner at the lower test temperatures, and essentially none in the shorter (higher temperature) tests.

The monolithic converter plugging mechanism suggested here differs in some important respects from the mechanism proposed by Ethyl Corporation (4). Ethyl found that the threshold exhaust gas temperature for converter plugging was about 816°C, while plugging occurred in our tests at temperatures as low as 706°C. Ethyl reported that some form of manganese, probably  $MnO$ , reacted with the monolithic substrate to form manganese silicate.  $Mn_3O_4$  then formed dendritic needles by a sintering reaction. We were not able to identify  $MnO$  in any of our converter deposits, even in tests run with less than the stoichiometric amount of oxygen in the exhaust. Furthermore, the alumina layer on the converter was not broken to expose the substrate to manganese oxide. If converter plugging depended on a reaction of manganese oxide with the catalyst support, plugging should have occurred much more rapidly in the test with the "nuncatalytic" converter, in which the support was completely exposed to the manganese oxide. However, plugging occurred at about the same rate with the "nuncatalytic" converter as with a production converter in which the support was covered with alumina and the catalytic metals.

Our tests have also refuted suggestions that plugging was due to reactions of the manganese oxide with elements from the engine oil or with components of the fuel detergent package.

POTENTIAL FOR MONOLITHIC CONVERTER PLUGGING IN CUSTOMER SERVICE - These engine dynamometer tests have shown that, when gasoline contains MMT, monolithic converter plugging on the Chevrolet 4.1-L California engine can occur at exhaust gas (catalyst inlet) temperatures which are experienced to some extent by most cars. However, this engine-converter combination is presently used only on cars sold in California, and as mentioned earlier, California has recently banned the use of MMT in that state. In addition, the Federal government has reduced the maximum allowable concentration of MMT in gasoline nationwide. These actions will significantly reduce, but not eliminate, the potential for monolithic converter plugging. It should be noted that some automobile manufacturers use monolithic

converters on all of their cars, not just in California.

**OTHER MMT EFFECTS** - Although the purpose of this test program was to study monolithic converter plugging, some information was obtained on plugging of bead-type converters, spark plug life, and exhaust hydrocarbon emissions. These items are discussed in Appendix B.

**REMOVAL OF DEPOSITS FROM A PLUGGED MONOLITHIC CONVERTER** - While this study was in progress, a service procedure was developed to remove the manganese oxide deposits from a plugged monolithic converter. The cleaning can be done without removing the plugged converter from the car. The procedure and results are presented in Appendix C.

## SUMMARY

The effects of fuel, oil, and engine operating variables on plugging of close-coupled monolithic converters were investigated in steady-state engine-dynamometer tests with MMT-containing fuel. The major findings are as follows:

1. Only the exhaust gas temperature and the MMT concentration in the fuel significantly affected the rate of converter plugging.

- a. Plugging occurred more rapidly as the exhaust gas temperature at the catalyst inlet was increased from 706°C to 843°C.

- b. Plugging time was inversely proportional to the manganese concentration in the fuel, over the range of 0.008 to 0.033 g Mn/L.

2. Converter plugging was not affected by a change in base fuel and detergent additive, or by a change in engine oil from a commercial SE-quality oil to an experimental ashless and phosphorus-free oil.

3. Converter plugging occurred as readily with a monolithic substrate containing no catalytic material as with a production catalyst consisting of the monolithic substrate coated with alumina, on which the catalytic metals (platinum and palladium) were deposited.

4. The deposits which plugged the converter were composed primarily of  $Mn_2O_4$ .

5. No evidence of any chemical reaction between the manganese oxide and the catalyst was found.

## CONCLUSION

Monolithic converter plugging appears to be a physical, rather than a chemical phenomenon, in which the manganese oxide collects primarily on the inlet edge of the converter.

## ACKNOWLEDGMENT

Many people made significant contributions to this program. E. J. Grates set up and maintained the emissions analyzers and sampling systems. E. J. Grates and E. G. Malzahn operated and maintained the engines and recorded the data. R. J. Belling, S. L. Clark, S. A. Jett, E. E. Klusendorf, J. D. LaMothe, and H. A. Nielsen installed the engines and helped monitor the tests. D. L. Hilden made the exhaust particulate measurements. J. C. Ulicny prepared the catalyst samples for analysis. F. A. Forster, J. J. Schultz, and H. E. Vargoser analyzed the converter deposits. A. C. Ottolini performed the electron microprobe studies. C. R. Stricklin determined the melting points of the deposits. J. R. Mondt supplied the bare-wire thermocouple. W. R. Leppard, N. A. Schilke, E. D. Klomp, T. A. Morel, and R. B. Rask were very helpful in discussions of exhaust flow characteristics. C. G. Mitsopoulos participated in the development of the catalyst cleaning procedure.

The catalytic converters were provided by AC Spark Plug Division.

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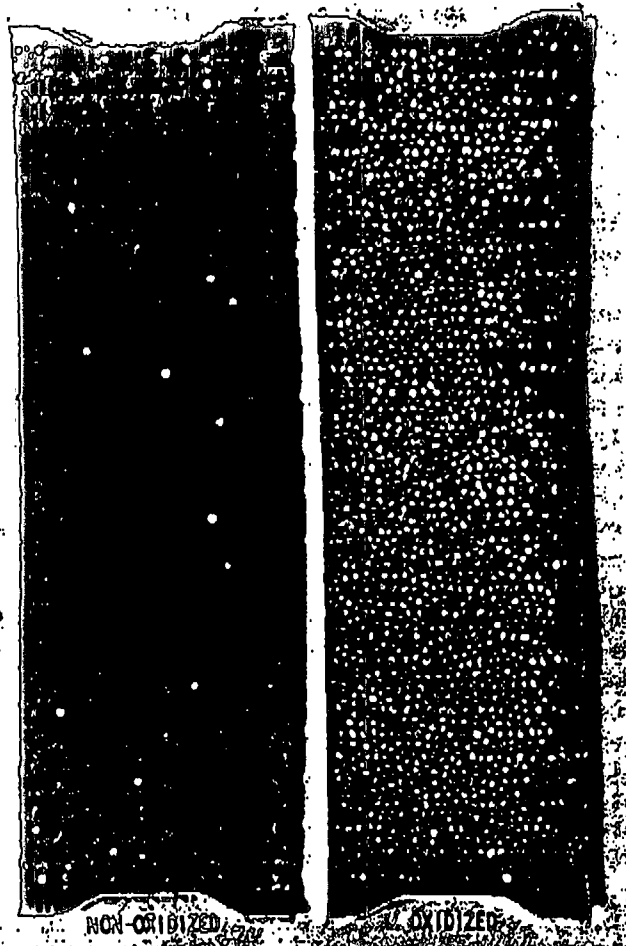


Fig. B-1 - Lower retainers from a non-oxidized and a severely oxidized band-type converter

plugging program. In the first plugging test, which began with a clean engine, the hydrocarbon emissions increased as shown in Figure B-2. The increase in engine emissions probably resulted from increasing exhaust pressure and accumulation of combustion chamber deposits. (The engine hydrocarbon emissions did not return all the way to their initial level when the spark plugs and converter were replaced.) As the test progressed, the conversion efficiency of the monolithic catalyst decreased only slightly, from about 85 percent initially to 80 percent at 130 hours.

Before the second test engine was operated on manganese-containing fuel, a monolithic converter was aged at an exhaust temperature of 829°C using fuel without MMT to evaluate the performance of the converter in the absence of MMT. The warmed-up steady-state hydrocarbon conversion efficiency, measured at an exhaust gas temperature of 732°C, was initially about 77 percent, declining to 71 percent in 140 hours and 62 percent in 350 hours. This test showed that, in the absence of MMT, the converter maintained reasonable efficiency for a longer period of time than was required to plug the converter when MMT was present in the fuel.

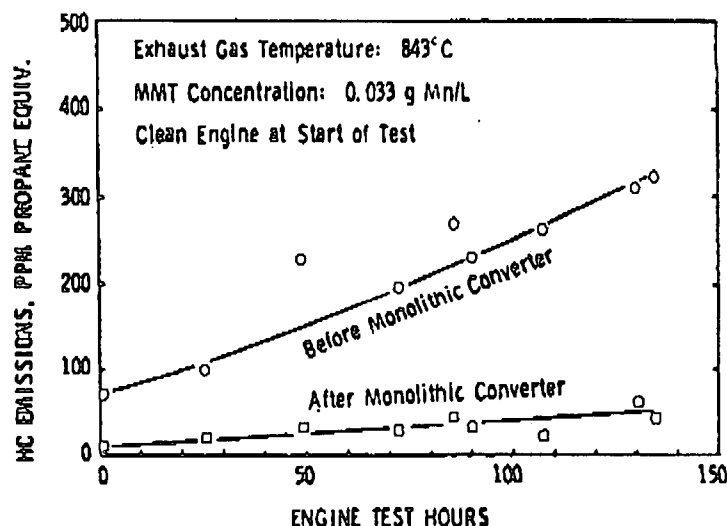


Fig. B-2 - Hydrocarbon emissions during a catalyst plugging test

### Appendix C

#### REMOVAL OF DEPOSITS FROM A PLUGGED MONOLITHIC CONVERTER

While the engine dynamometer study of converter plugging was in progress, a service procedure was developed to remove the manganese oxide deposits from a plugged monolithic converter. The cleaning can be done without removing the converter from the car. A 1977 Chevrolet Nova equipped with a 4.1-L six-cylinder engine and California emission control system was used for the tests. The cleaning procedure and results are described in the following sections.

**CLEANING SOLUTION** - Laboratory tests were conducted with several different acids and other potential cleaning agents. Based on the results of those tests, it was concluded that hot, dilute (3N) hydrochloric acid (HCl) would be a good solution for removing the converter deposits. The hot acid would dissolve the deposits, but would cool quickly enough to prevent damage to the converter.

**CLEANING PROCEDURE** - A 1.3-mm diameter hole was drilled in the top of the exhaust manifold directly above the monolithic converter. A 1.6-mm diameter hole was drilled in the bottom of the converter to provide drainage during the cleaning process. The right front corner of the car was raised with a jack so that the cleaning solution would not run down the exhaust pipe, but would drain out the hole in the bottom of the converter.

The 3N HCl solution (100 ml) was heated to about 95°C in an Erlenmeyer flask, and then transferred to a plastic laboratory wash bottle. With the plugged monolithic converter at ambient temperature, the acid was added slowly through the hole in the exhaust manifold over a period of about 10 minutes. The acid

was directed at the manganese oxide deposits on the converter, rather than being allowed to run down the walls of the manifold.

About 10 minutes after the acid was applied, a strong stream of water from a hose was directed through the hole in the manifold toward the top of the converter. The effluent from the bottom of the converter had a reddish-brown color, indicating that some of the deposits had not dissolved completely, but were softened and loosened sufficiently to be flushed from the catalyst. Flushing was continued until the effluent was nearly clear. About four litres of water were used.

Compressed air directed at the top of the converter for a few seconds removed most of the water.

Converters which were about 50 percent plugged were easily cleaned by 100 ml of acid. However, an 80 percent plugged converter required 300 ml of acid to remove all of the deposits.

After the cleaning procedure was completed, the holes in the top of the manifold and the bottom of the converter were closed by welding steel pipe fittings to the manifold and converter, and inserting threaded pipe plugs to form air-tight seals.

Table C-1. Monolithic Converter Pressure Drop

Engine RPM	Pressure Drop Across Converter, kPa		
	New	Plugged	Cleaned
1600	5.2	15.2	5.7
2000	8.9	23.0	8.4
2400	10.6	29.7	11.1
2800	13.0	34.4	12.5
3200	14.7	39.8	14.2
3600	15.5	42.6	15.2
4000	16.5	45.3	15.9

**RESULTS** - Three converters were cleaned by this procedure. Two were about 50 percent plugged from engine dynamometer tests, and the third was about 80 percent plugged from a vehicle test. Only the results with the 80 percent plugged converter are discussed here.

**Exhaust Pressure** - The pressure drop across a new converter, the converter which was 80 percent plugged, and the same converter after cleaning, were measured with the car operating on a test track at various engine speeds at wide-open-throttle. The results are presented in Table C-1.

These data show that the cleaning procedure reduced the pressure drop across the plugged converter to essentially that of a new converter.

**Exhaust Emissions** - It was important to determine what effect the cleaning procedure might have on catalyst efficiency. Therefore, exhaust emission tests, using the 1975 Federal Test Procedure, were run with the new converter, the plugged converter, and the cleaned converter. Emissions were measured simultaneously at the exhaust manifold ahead of the converter and at the tailpipe. During these tests, the beads were removed from the bead-type converter, so that the efficiency of the monolithic converter could be determined. Removal of the beads probably changed the exhaust pressure and may have affected the engine emissions slightly, but the catalyst efficiency should not have been significantly affected. The emission results are shown in Table C-2.

The conversion efficiency of the plugged converter increased after cleaning. Removing the deposits from the catalyst opened the channels of the monolith which were plugged, and exposed more catalytic surface area. The HC and CO conversion efficiencies after cleaning were not as high as those of the new converter. However, the plugged converter must be expected to suffer some loss in activity from

Table C-2. Exhaust Emissions (1975 FTP) with New, 80% Plugged, and Cleaned Converters

	HC, g/mile			CO, g/mile			NO <sub>x</sub> , g/mile		
	New	Plugged	Cleaned	New	Plugged	Cleaned	New	Plugged	Cleaned
Ahead of Converter	1.21	1.36	1.32	14.69	17.65	15.03	1.37	1.07	1.23
Tailpipe <sup>a</sup>	0.25	0.55	0.42	2.80	7.50	4.98	1.32	1.04	1.18
Catalyst Efficiency, %	79	59	68	81	57	67	NA	NA	NA
Eff. of Similar Converter Aged Without MMT, %			62			66			

<sup>a</sup> The beads were removed from the bead-type converter.

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the initial level simply due to aging. Therefore, Table C-2 also shows the HC and CO efficiencies of a converter on a vehicle which operated without MMT for about the same distance and over the same driving schedule as the car with the plugged converter (1). Thus, the cleaning procedure restored the plugged converter to the condition it would have been in if plugging had not occurred. Obviously, the activity loss due to aging could not be reversed.

SUMMARY - The cleaning procedure was effective in removing the manganese oxide deposits from a plugged monolithic converter, it was performed without removing the converter from the car, and it did not reduce the catalyst conversion efficiency. If converter plugging in customer service should become a problem, this cleaning procedure may be useful. Service personnel would be provided with instructions for safe handling of the cleaning solution.